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⑤④ **Process for improving the octane number of cracked gasolines.**

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⑦③ Proprietor : **MOBIL OIL CORPORATION**  
**150 East 42nd Street**  
**New York New York 10017 (US)**

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⑦② Inventor : **Morrison, Roger Allan**  
**P.O. Box A-284**  
**Deptford New Jersey 08096 (US)**

⑧④ Designated Contracting States :  
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⑦④ Representative : **Cooper, John Anthony et al**  
**Mobil Court 3 Clements Inn**  
**London WC2A 2EB (GB)**

⑤⑥ References cited :  
**EP-A- 0 093 477**  
**DE-A- 3 341 736**  
**FR-A- 2 245 755**  
**US-A- 3 843 741**

**EP 0 235 416 B1**

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## Description

This invention relates to a process for upgrading the octane number of a gasoline-boiling fraction.

Reforming naphthas which are paraffinic and/or naphthenic to increase the octane number is well known. Such reforming is traditionally carried out with platinum reforming catalysts and is a widely used commercial refinery process.

Naphtha fractions, which are not particularly naphthenic or which may contain substantially no naphthenes at all, can be aromatized in good, commercially acceptable yields by contacting such feeds, under relatively severe conditions, with ZSM-5 and related crystalline aluminosilicate zeolite catalysts. Highly aromatic liquid yields of upwards of 30 percent have been achieved.

This process converts a predominantly aliphatic feed and operates at 343 to 816°C (650° to 1500°F) at a space velocity of about 1 to 15 WHSV.

In a similar process, aromatic containing feeds, such as reformates, have had their aromatic contents increased by contact with ZSM-5 and related intermediate pore zeolites. This process selectively cracks aliphatics in the feed to produce active fragments at least some of which alkylate existing aromatics and increase the aromatic content while decreasing the low octane paraffin content. This process converts feed rich in aromatics and operates at 260 to 538°C (500° to 1000°F).

The operating conditions in both processes overlap some, as do the feeds. It is probable that some cracking-alkylation and some aromatization take place in both processes. The distinction between the processes is perhaps better expressed as one of conversion predominance with the more severe conditions favoring new aromatic ring formation and the less severe conditions favoring alkylation of preformed or newly created aromatic rings.

In either case, the processes are improved when the ZSM-5 catalyst is modified to include up to 10 weight percent zinc or cadmium, or other similar promoting metal. Such metal is suitably incorporated with the zeolite by cation exchange, impregnation and/or vapor deposition. Further inclusion of copper into such a catalyst reduces loss during regeneration of zinc and/or cadmium.

The following patents comprise a partial list of those patents directed to processes described above.

EP 0 093 477 A2 describes a low severity process for preparing a benzene-toluene-xylene enriched stream from a feed stream containing a by-product effluent of a process for the pyrolytic cracking of hydrocarbons. The process comprises contacting the feed stream with a ZSM-5-type catalyst under low severity conditions.

U.S. Patent 3,756,942 discloses increasing the aromatic content of a light gasoline formed by fluid catalytic cracking (FCC) by conversion of the gasoline over ZSM-5 zeolite.

U.S. Patent 3,760,024 discloses a process for producing aromatic compounds by contacting C<sub>2</sub>-C<sub>4</sub> paraffins, olefins or mixtures with ZSM-5.

U.S. Patent 3,775,501 discloses improving the yield of aromatics from a hydrocarbon feed selected from the group consisting of aliphatic olefins and paraffins by contacting the hydrocarbon feed in air or oxygen with a zeolite such as ZSM-5.

U.S. Patent 3,827,968 discloses contacting C<sub>2</sub>-C<sub>5</sub> olefins with ZSM-5 under such conditions as to oligomerize the olefins and subsequently passing the oligomerized olefins over ZSM-5 at aromatizing conditions to form a product having an enhanced aromatic content.

U.S. Patent 3,890,218 discloses upgrading the octane number of hydrocarbon fractions boiling in the naphtha range and having a low octane number by contacting the naphtha fraction over an intermediate pore zeolite such as ZSM-5 in which the activity of the zeolite has been modified such as by steaming so as to increase the high octane liquid yield by shape selective cracking-alkylation mechanism and an aliphatic hydrocarbon aromatization process. The process is preferably operated at conditions which are intermediate between the optimum conditions for the respective conversion mechanisms. Among the feeds which are useful in the aforementioned patent are cracked gasolines. The preferred feeds are hydrocarbon compositions containing 0 to 20 wt. % aromatics, predominantly C<sub>6</sub>-C<sub>8</sub> aromatics, and 60 to 100 wt. % straight and branched chain paraffins and olefins with minimal amounts of naphthenes.

U.S. Patent 3,953,366 discloses aromatization and alkylation of aromatic rings by contacting a hydrocarbon feed such as a cracked gasoline fraction with ZSM-5 and related zeolites which has rhenium deposited thereon.

U.S. Patent 3,960,978 discloses converting gaseous C<sub>2</sub>-C<sub>5</sub> olefins to an olefinic gasoline by passing the olefin feed over ZSM-5. The zeolite can be steamed to a low alpha activity value.

U.S. Patent 4,021,502 discloses producing a gasoline by passing a feed stock of C<sub>2</sub>-C<sub>6</sub> olefins or mixtures with C<sub>1</sub>-C<sub>5</sub> paraffins over ZSM-4, ZSM-12, ZSM-18, chabazite or zeolite beta.

U.S. Patent 4,227,992 discloses separating ethylene from light olefins by contact with ZSM-5 under con-

ditions such that the  $C_3+$  olefins are converted to both gasoline and fuel oil.

U.S. Patent 4,396,497 describes the treatment of gasoline boiling range hydrocarbons to increase the octane number thereof by contact with a gamma alumina catalyst.

Another process recently used to increase the octane of gasoline boiling fractions involves the addition of ZSM-5 and related intermediate pore zeolites to the conventional cracking catalyst such as zeolites of the X or Y faujasite variety during the cracking of gas oils to gasoline products. Examples of patents which describe such a process include U.S. Patent Nos. 3,894,931 ; 3,894,903 ; and 3,894,934.

One important consideration involved in the upgrading of gasoline fractions in addition to boosting the octane number thereof is obtaining the highest possible liquid yield. Thus, although the technology referred to above is excellent in upgrading the quality of gasoline boiling range fragments, hydrocarbon conversion over ZSM-5 under cracking, alkylation or aromatizing conditions has resulted in substantial loss of gasoline yield in the form of light gases, i.e.,  $C_1-C_4$ .

It would be beneficial if a process were available which could improve the octane number of a gasoline boiling fraction without excessive yield loss.

A way has now been discovered to increase the octane number of cracked gasoline without substantial yield loss.

Accordingly, the present invention provides a process for improving the octane number of gasoline characterized by contacting a gasoline containing at least 20 wt percent olefins with an acidic crystalline zeolite catalyst at 343 to 510°C (650 to 950°F), in the absence of hydrogen, at a pressure from atmospheric to 450 kPa wherein the amount and acidity of the catalyst increase the octane number of the gasoline by 1.0 octane number, and a yield loss of less than 5.0 wt percent gasoline.

Figure 1 is a plot illustrating increased octane versus make of  $C_1-C_4$  after treating an FCC gasoline with five types of acid zeolite catalysts in fixed-bed operation.

Figure 2 is a plot illustrating the same relationship as in Figure 1 with a ZSM-12 catalyst having widely different alpha values.

Figure 3 is a plot similar to Figure 2 for a ZSM-5 catalyst.

Figure 4 is a graph illustrating the same relationship as in Figures 1-3 with steamed and unsteamed ZSM-12 and steamed ZSM-5 catalysts.

Figure 5 is a plot illustrating the variations in the changes in octane number as a function of  $C_1-C_4$  make for various FCC and TCC gasolines with steamed ZSM-12 catalysts.

Figure 6 is a graph illustrating the effect of process variables on the change in octane versus  $C_1-C_4$  make upon fixed bed treatment of several FCC and TCC gasolines with several zeolite catalysts.

The process of the present invention increases the octane number of gasoline boiling fractions with only minimal, i.e., less than 5 wt.%, yield loss, typically less than 1 wt.% yield loss. The yield loss is in the form of  $C_1-C_4$  gas make.

The gasoline feed is passed through a fixed bed of acidic crystalline aluminosilicate zeolite catalysts for conversion of the gasoline feed to a gasoline product of improved octane number. Suitable temperatures include 343 to 510°C (650 to 950°F). Better results are achieved at 357 to 496°C (675 to 925°F). The preferred operating temperatures are 371 to 482°C (700° to 900°F), preferred space velocities are at least about 10 WHSV and the pressure is atmospheric to 450 kPa (50 psig). The process is run in the absence of hydrogen.

Suitable feeds include any FCC or TCC gasoline. Thus, any 24 to 121°C (75 to 250°F) low end point FCC gasoline ; 24 to 154°C (75 to 310°F) distillate range FCC gasoline or full range 24 to 218°C (75 to 425°F) TCC or FCC gasolines or fractions thereof are applicable in this invention. Such gasolines generally have olefin contents of at least 20 wt.%. Depending on where such gasoline is cut, olefin contents of at least 30 wt.% and 40 wt.% are typical. Other useful gasolines which can be upgraded include gasolines obtained from conversion of methanol to aromatic gasoline over zeolite catalysts, oligomerization of olefins over intermediate pore zeolites to olefinic gasolines, pyrolysis gasoline, etc.

The octane increase obtained via the present invention is more readily seen in the low end point gasolines, i.e., 24 to 121°C (75 to 250°F) and 24 to 154°C (75 to 310°F) cracked gasolines. This result is consistent with an olefin isomerization reaction mechanism inasmuch as the lighter weight gasolines contain a greater olefin concentration (typically comprising about 50 wt.%) than full range gasolines. Thus, it has been found that at about 1 wt.% gasoline yield loss, i.e.,  $C_1-C_4$ , upon conversion over the zeolite catalyst useful in this invention, the octane increase of the product relative to feed is about :

2-2.5 R+O for 24 to 121°C (75 to 250°F) FCC gasoline

1.5-2 R+O for 24 to 154°C (75 to 310°F) Distillate mode FCC gasoline

1-1.5 R+O for full range 24 to 218°C (75 to 425°F) TCC or FCC gasolines

Gasoline yield losses are primarily due to  $C_1-C_4$  gas make. However, over 90% of these light gases

comprise C<sub>3</sub>-C<sub>4</sub> olefins which, after alkylation with isobutane, can be added to the gasoline pool to increase gasoline yields and further improve octane number.

Catalysts useful in the present invention can be chosen from any acid catalyst, although, intermediate pore size aluminosilicate zeolites are preferred. Such preferred catalysts have relatively low aging rates.

Zeolites useful for the crystalline aluminosilicate component of this invention include the acidic forms of : zeolite X, described in U.S. Patent 2,882,244 ; zeolite Y, described in U.S. Patent 3,130,007 ; mordenite; zeolite L, described in U.S. Patent 3,216,789 ; zeolite T, described in U.S. Patent 2,950,952 ; and zeolite beta, described in U.S. Patent 3,308,069.

The preferred catalysts are crystalline aluminosilicate zeolites which are intermediate pore size zeolites. Such zeolites have a constraint index of 1 to 12 and have a silica to alumina framework ratio of at least 12 and preferably at least about 30.

The intermediate pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and other similar materials.

ZSM-5 is described in U.S. Patent No. 3,702,886.

ZSM-11 is described in U.S. Patent No. 3,709,979.

ZSM-12 is described in U.S. Patent No. 3,832,449.

ZSM-23 is described in U.S. Patent No. 4,076,842.

ZSM-35 is described in U.S. Patent No. 4,016,245.

ZSM-38 is described in U.S. Patent No. 4,046,859.

ZSM-48 is described in U.S. Patent No. 4,375 573.

The intermediate pore zeolites are preferred. Thus, ZSM-12 and zeolite beta although useful, are not necessarily preferred.

To avoid substantial cracking of the paraffin and olefin contents of the gasoline and subsequent aromatization, the activity of the catalyst must be within a critical range. Accordingly, the acid activity of the catalyst should be from 5 to 100, preferably the alpha is 5 to 75, most preferably 10 to 50. Any conventional method may be used to attain desired acid activity of the zeolite catalysts, e.g., extensive base exchange with alkali metal cations, synthesis with high silica to alumina framework ratios, zeolite dilution in matrix and steaming. Steaming of acid in zeolites is the preferred method.

The alpha value of a crystalline aluminosilicate zeolite is related to the activity of the catalyst for cracking normal hexane. The alpha value from a hexane-cracking test can be determined in accordance with the method set forth by P.B. Weisz and J.N. Miale in Journal of Catalysis, Vol. 4, No. 4, August 1969, pages 527-529.

In all examples, the catalysts were 0.25 to 0.85 mm (sized to pass through 20x60 mesh sieves) and pretreated in flowing hydrogen at 482°C (900°F) for 1 hour prior to use. The catalyst was heated to operating temperature, and charge run over the hot catalyst at atmospheric pressure plus the pressure drop across the catalyst bed. There was no added gas.

Material balances were made by collecting product in a liquid nitrogen-cooled trap and subsequent expansion of the gases into a precalibrated, constant volume system. Liquid and gas analysis was by gas chromatography. The liquid product for octane determination was collected in ice followed by a dry ice-acetone trap system. No distillation was done since most of the runs involved less than 1% C<sub>1</sub>-C<sub>4</sub> make. However, where the gas make was greater than 1%, a correction was made in the reported octane value in order to discount light gas dissolved in the liquid. This correction is about 0.1 R+O for each 1% C<sub>1</sub>-C<sub>4</sub> make and has been made in the Figures.

#### EXAMPLE 1

Various zeolites, e.g., ZSM-5, -11, -12, -23, and zeolite beta were used to upgrade a full range FCC gasoline 24 to 218°C (75 to 425°F) having the composition by weight shown in Table 1. Each catalyst was tested at 371 to 482°C (700° to 900°F). Tables 2-4 illustrate the gasoline product composition at two of such tested temperatures for each zeolite. The improvement in octane number relative to yield loss is shown in Fig. 1 for each zeolite. The optimum improvement in octane numbers lies around 1% C<sub>1</sub>-C<sub>4</sub> make.

FULL RANGE FCC GASOLINETABLE 1

5	C <sub>1</sub>	
	C <sub>2</sub>	
	C <sub>2</sub> =	
	C <sub>3</sub>	
10	C <sub>3</sub> =	
	ISO-C <sub>4</sub>	0.03
	N-C <sub>4</sub>	0.20
	C <sub>4</sub> =	0.57
	ISO-C <sub>5</sub>	7.96
15	N-C <sub>5</sub>	-
	C <sub>5</sub> =	8.61
	2,2 DM-C <sub>4</sub>	0.10
	CYCLO-C <sub>5</sub>	0.68
	2,3 DM-C <sub>4</sub>	0.69
20	2-M-C <sub>5</sub>	4.16
	3-M-C <sub>5</sub>	2.24
	N-C <sub>6</sub>	1.08
	C <sub>6</sub> =	3.53
	M-CYCLO-C <sub>5</sub>	2.67
25	BENZENE	1.51
	CYCLO-C <sub>6</sub>	0.34
	C <sub>7</sub> 'S	11.95
	N-C <sub>7</sub>	-
	TOLUENE	4.73
	C <sub>8</sub> 'S	6.59
30	N-C <sub>8</sub>	-
	C <sub>8</sub> AR.	9.85
	C <sub>9</sub> + PAR.	-
	C <sub>9</sub> AR.	9.85
	C <sub>10</sub> AR.	8.39
35	C <sub>10</sub> -C <sub>12</sub> AR.	14.27
	NAPHTHALENE	-
	M-NAPHTHALENE	-
	C <sub>13</sub> +'S	-
40	R+O, Octane number	89.20
45		
50		
55		

TABLE 2

5	CATALYST	ZSM-5 <sup>1</sup>	ZSM-5	ZSM-12 <sup>2</sup>	ZSM-12
	TEMPERATURE, °C (°F)	372 (702)	427 (800)	468 (875)	454 (850)
5	PRESSURE, PSIG	30.00	50.00	30.00	30.00
	kPa	310	450	310	310
	WHSV	10.00	10.00	10.00	10.00
	TIME ON STREAM, HRS.	23.40	164.50	23.80	119.50
10	PRODUCT DIST., WT %				
	C <sub>1</sub>	0.00	0.00	0.02	0.00
	C <sub>2</sub>	0.00	0.00	0.05	0.02
	C <sub>2</sub> =	0.01	0.02	0.04	0.01
15	C <sub>3</sub>	0.01	0.02	0.04	0.01
	C <sub>3</sub> =	0.31	1.12	0.84	0.08
	ISO-C <sub>4</sub>	0.03	0.08	0.04	0.03
	N-C <sub>4</sub>	0.15	0.18	0.18	0.17
	C <sub>4</sub> =	0.83	1.92	1.47	0.49
	ISO-C <sub>5</sub>	6.68	7.70	6.97	6.79
20	N-C <sub>5</sub>	0.15	0.35	0.16	0.13
	C <sub>5</sub> =	7.96	9.06	8.54	8.04
	2,2 DM-C <sub>4</sub>	0.02	0.11	0.07	0.10
	CYCLO-C <sub>5</sub>	0.66	0.68	0.67	0.65
	2,3 DM-C <sub>4</sub>	0.65	0.63	0.67	0.69
25	2-M-C <sub>5</sub>	3.87	3.95	4.04	3.95
	3-M-C <sub>5</sub>	2.09	2.11	2.17	2.17
	N-C <sub>6</sub>	1.04	1.06	1.11	1.06
	C <sub>6</sub> =	3.21	2.89	3.20	3.41
	M-CYCLO-C <sub>5</sub>	2.80	2.78	2.82	2.73
30	BENZENE	1.47	1.42	1.47	1.50
	CYCLO-C <sub>6</sub>	0.39	0.33	0.32	0.30
	C <sub>7</sub> 'S	11.90	11.05	11.51	12.19
	N-C <sub>7</sub>	0.00	0.00	0.00	0.00
	TOLUENE	4.67	4.67	4.76	4.84
	C <sub>8</sub> 'S	6.98	6.06	6.23	6.79
35	N-C <sub>8</sub>	0.00	0.00	0.00	0.00
	C <sub>8</sub> AR.	10.20	9.71	10.02	10.21
	C <sub>9</sub> + PAR.	0.00	0.00	0.00	0.00
	C <sub>9</sub> AR.	10.09	9.51	9.74	10.17
	C <sub>10</sub> AR.	8.78	8.30	8.41	8.71
40	C <sub>10</sub> -C <sub>12</sub> AR.	15.04	14.30	14.45	14.79
	NAPHTHALENE	0.00	0.00	0.00	0.00
	M-NAPHTHALENE	0.00	0.00	0.00	0.00
	C <sub>13</sub> + 'S	0.00	0.01	0.00	0.00
	WT % CONV, TOTAL	2.42	4.61	3.46	2.56
45	TO C <sub>1</sub> -C <sub>4</sub>	0.74	2.68	1.96	0.26
	R+O (CHARGE = 89.2)	90.80	91.10	91.40	89.70

1. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 70; steamed alpha = 10  
 2. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 54; steamed alpha = 11

50

55

TABLE 3

5	CATALYST	ZSM-11 <sup>3</sup>	ZSM-11	ZSM-23 <sup>4</sup>	ZSM-23
	TEMPERATURE, °C	399	399	481	428
5	(°F)	(750)	(750)	(898)	(802)
	PRESSURE, PSIG	30.00	30.00	30.00	30.00
5	kPa	310	310	310	310
	WHSV	10.00	10.00	10.00	10.00
5	TIME ON STREAM, HRS.	21.40	45.30	22.90	97.40
10	PRODUCT DIST., WT %				
15	C <sub>1</sub>	0.00	0.02	0.00	0.00
	C <sub>2</sub>	0.00	0.05	0.04	0.00
15	C <sub>2</sub> =	0.02	0.01	0.23	0.02
	C <sub>3</sub>	0.00	0.14	0.16	0.00
15	C <sub>3</sub> =	0.79	0.42	2.48	0.54
	ISO-C <sub>4</sub>	0.03	0.20	0.10	0.02
15	N-C <sub>4</sub>	0.22	0.21	0.19	0.15
	C <sub>4</sub> =	1.62	1.20	2.83	1.07
20	ISO-C <sub>5</sub>	6.06	5.90	6.27	6.35
	N-C <sub>5</sub>	0.16	0.12	0.15	0.13
20	C <sub>5</sub> =	10.04	9.87	6.97	7.86
	2,2 DM-C <sub>4</sub>	0.00	0.00	0.01	0.06
20	CYCLO-C <sub>5</sub>	0.84	0.84	0.64	0.67
	2,3 DM-C <sub>4</sub>	0.56	0.57	0.71	0.70
25	2-M-C <sub>5</sub>	3.47	3.44	3.60	3.89
	3-M-C <sub>5</sub>	1.74	1.74	2.04	2.09
25	N-C <sub>6</sub>	1.26	1.27	1.04	1.08
	C <sub>6</sub> =	3.69	3.75	2.46	3.19
25	M-CYCLO-C <sub>5</sub>	2.91	2.92	2.47	2.79
	BENZENE	1.79	1.82	1.42	1.48
30	CYCLO-C <sub>6</sub>	0.50	0.50	0.28	0.40
	C <sub>7</sub> 'S	11.06	11.28	10.40	11.91
30	N-C <sub>7</sub>	0.00	0.00	0.00	0.00
	TOLUENE	4.96	5.01	4.97	4.70
35	C <sub>8</sub> 'S	6.17	6.32	6.18	6.75
	N-C <sub>8</sub>	0.00	0.00	0.00	0.00
35	C <sub>8</sub> AR.	9.03	9.10	10.59	10.19
	C <sub>9</sub> + PAR.	0.00	0.00	0.00	0.00
35	C <sub>9</sub> AR.	9.95	10.07	10.14	9.98
	C <sub>10</sub> AR.	8.23	8.35	8.64	8.68
40	C <sub>10</sub> -C <sub>12</sub> AR.	14.91	15.11	14.97	15.31
	NAPHTHALENE	0.00	0.00	0.00	0.00
40	M-NAPHTHALENE	0.00	0.00	0.00	0.00
	C <sub>13</sub> + 'S	0.00	0.00	0.00	0.00
45	WT % CONV, TOTAL	3.96	3.56	6.97	3.01
	TO C <sub>1</sub> -C <sub>4</sub>	1.93	1.31	5.33	1.19
45	R+O (CHARGE = 89.2)	92.80	92.30	91.40	90.80
50	3. Steamed alpha = 13.				
	4. Steamed alpha = 11.				

TABLE 4

	CATALYST	BETA <sup>5</sup>	BETA
	TEMPERATURE, °C	454	482
	(°F)	(850)	(899)
6	PRESSURE, PSIG	30.00	30.00
	kPa	310	310
	WHSV	10.00	10.00
	TIME ON STREAM, HRS.	21.80	45.80
10	PRODUCT DIST., WT %		
	C <sub>1</sub>	0.00	0.02
	C <sub>2</sub>	0.05	0.11
	C <sub>2</sub> =	0.02	0.05
15	C <sub>3</sub>	0.03	0.14
	C <sub>3</sub> =	0.09	0.19
	ISO-C <sub>4</sub>	0.03	0.03
	N-C <sub>4</sub>	0.17	0.20
	C <sub>4</sub> =	0.45	0.59
	ISO-C <sub>5</sub>	6.51	6.57
20	N-C <sub>5</sub>	0.15	0.15
	C <sub>5</sub> =	7.72	7.83
	2,2 DM-C <sub>4</sub>	0.14	0.04
	CYCLO-C <sub>5</sub>	0.79	0.74
	2,3 DM-C <sub>4</sub>	0.70	0.69
25	2-M-C <sub>5</sub>	3.76	3.77
	3-M-C <sub>5</sub>	2.09	2.07
	N-C <sub>6</sub>	0.93	0.94
	C <sub>6</sub> =	3.58	3.49
	M-CYCLO-C <sub>5</sub>	2.64	2.63
30	BENZENE	1.46	1.41
	CYCLO-C <sub>6</sub>	0.42	0.45
	C <sub>7</sub> 'S	11.94	11.88
	N-C <sub>7</sub>	0.00	0.00
	TOLUENE	4.81	4.81
	C <sub>8</sub> 'S	7.05	6.88
35	N-C <sub>8</sub>	0.00	0.00
	C <sub>8</sub> AR.	10.36	10.31
	C <sub>9</sub> + PAR.	0.00	0.00
	C <sub>9</sub> AR.	10.42	10.26
	C <sub>10</sub> AR.	8.82	8.77
40	C <sub>10</sub> -C <sub>12</sub> AR.	14.89	14.96
	NAPHTHALENE	0.00	0.00
	M-NAPHTHALENE	0.00	0.00
	C <sub>13</sub> + 'S	0.00	0.00
45	WT % CONV, TOTAL	2.44	2.36
	TO C <sub>1</sub> -C <sub>4</sub>	0.33	0.77
	R+O (CHARGE = 89.2)	90.40	90.10

5. H-Beta; SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40; steamed alpha = 6.



Table 5 illustrates the octane improvement for each of the tested zeolites at 1% gas make.

**TABLE 5**  
**Octane Improvement with Various**  
**Zeolites at 1% C<sub>1</sub>-C<sub>4</sub> Make**

Zeolite	Octane Improvements, R+O
ZSM-5	1.2
ZSM-11	0.7
ZSM-12	1.1
ZSM-23	1.3
Zeolite beta	0.9

At this level, all of the catalysts improve octane, suggesting that acidity alone will accomplish this chemistry.

In general, the light gases formed are olefinic. ZSM-5 is the best, yielding about 95% olefins vs about 90% for ZSM-12. In terms of activity, ZSM-5, -11, and -23, are 41.7 to 55.6°C (75 to 100°F) more active than ZSM-12 at similar alphas.

#### EXAMPLE 2

In this example, ZSM-5 and ZSM-12 contacted a full range FCC gasoline. Various alpha values for each catalyst were tested. The results are summarized in Figs. 2 (ZSM-12) and 3 (ZSM-5). Different space velocities were used for the ZSM-12 runs, but space velocity is not important nor does it effect conclusions on alpha variations.

The fresh ZSM-5 and ZSM-12 both aged rapidly, at more than 55.6°C (100°F)/100 hrs. Time On Stream (TOS). Aging may be due to nitrogen poisons, coking, or both. The relatively high temperatures should minimize nitrogen sorption, so coking is the more likely cause. At the other extreme, ZSM-12 with an alpha of 1 does not have sufficient activity to achieve all of the desired reactions. At moderate alphas, the yield/octane relationship is similar in the range of 10-30 with perhaps a slight advantage for an alpha of about 30 in octane improvement and activity.

#### EXAMPLE 3

ZSM-5 and ZSM-12 were used to improve the octane number of a full range TCC gasoline having the composition shown in Table 6. Tables 7-8 show the improved gasoline product composition.

TCC gasoline responds like FCC gasoline, as indicated by Fig. 4. The yield/octane ratio is 1 R+O/1% C<sub>1</sub>-C<sub>4</sub> make. At higher octane, ZSM-12 may be more effective than ZSM-5. One of the ZSM-12's used was a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=250, alpha=39 catalyst. The yield/octane was equivalent to that of the steamed catalysts, suggesting that lower activity via either steaming or use of a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is acceptable.

## FULL RANGE TCC GASOLINE

TABLE 6

5	C <sub>1</sub>	
	C <sub>2</sub>	
	C <sub>2</sub> =	
	C <sub>3</sub>	
	C <sub>3</sub> =	
10	ISO-C <sub>4</sub>	0.06
	N-C <sub>4</sub>	0.36
	C <sub>4</sub> =	0.80
	ISO-C <sub>5</sub>	10.50
	N-C <sub>5</sub>	1.74
	C <sub>5</sub> =	2.89
15	2,2 DM-C <sub>4</sub>	0.04
	CYCLO-C <sub>5</sub>	0.18
	2,3 DM-C <sub>4</sub>	1.08
	2-M-C <sub>5</sub>	4.44
	3-M-C <sub>5</sub>	2.81
20	N-C <sub>6</sub>	0.82
	C <sub>6</sub> =	1.26
	M-CYCLO-C <sub>5</sub>	2.69
	BENZENE	1.34
	CYCLO-C <sub>6</sub>	-
25	C <sub>7</sub> 'S	10.80
	N-C <sub>7</sub>	-
	TOLUENE	5.01
	C <sub>8</sub> 'S	6.18
	N-C <sub>8</sub>	-
30	C <sub>8</sub> AR.	10.70
	C <sub>9</sub> + PAR.	-
	C <sub>9</sub> AR.	10.91
	C <sub>10</sub> AR.	8.87
	C <sub>10</sub> -C <sub>12</sub> AR.	16.55
35	NAPHTHALENE	0.00
	M-NAPHTHALENE	0.00
	C <sub>13</sub> + 'S	0.00
	R+O	88.8

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TABLE 7

	CATALYST	ZSM-5 <sup>1</sup>	ZSM-5	ZSM-12 <sup>2</sup>	ZSM-12
	TEMPERATURE, °C	426	440	482	497
5	(°F)	(799)	(824)	(900)	(926)
	PRESSURE, PSIG	50.00	50.00	30.00	30.00
	kPa	450	450	310	310
	WHSV	10.00	10.00	10.00	10.00
	TIME ON STREAM, HRS.	23.20	170.90	71.30	95.30
10	PRODUCT DIST., WT %				
	C <sub>1</sub>	0.00	0.00	0.01	0.00
	C <sub>2</sub>	0.00	0.00	0.04	0.07
	C <sub>2</sub> =	0.00	0.00	0.03	0.06
15	C <sub>3</sub>	0.07	0.11	0.03	0.05
	C <sub>3</sub> =	0.62	0.87	0.42	0.75
	ISO-C <sub>4</sub>	0.18	0.44	0.05	0.06
	N-C <sub>4</sub>	0.43	0.49	0.34	0.34
	C <sub>4</sub> =	1.37	1.65	1.18	1.50
20	ISO-C <sub>5</sub>	10.46	10.42	9.44	9.10
	N-C <sub>5</sub>	1.71	1.75	1.74	0.13
	C <sub>5</sub> =	4.17	3.98	3.38	5.14
	2,2 DM-C <sub>4</sub>	0.03	0.04	0.04	0.06
	CYCLO-C <sub>5</sub>	0.26	0.65	0.20	0.46
25	2,3 DM-C <sub>4</sub>	0.98	0.76	1.05	0.82
	2-M-C <sub>5</sub>	4.21	4.15	4.41	4.28
	3-M-C <sub>5</sub>	2.67	2.66	2.79	2.80
	N-C <sub>6</sub>	0.78	0.77	0.81	0.81
	C <sub>6</sub> =	1.21	1.22	1.26	1.29
	M-CYCLO-C <sub>5</sub>	2.74	2.70	2.79	2.71
30	BENZENE	1.14	1.09	1.11	1.18
	CYCLO-C <sub>6</sub>	0.22	0.28	0.28	0.23
	C <sub>7</sub> 'S	10.60	10.42	10.85	10.74
	N-C <sub>7</sub>	0.00	0.00	0.00	0.00
	TOLUENE	5.11	4.97	5.16	5.18
35	C <sub>8</sub> 'S	5.92	5.85	6.06	5.88
	N-C <sub>8</sub>	0.00	0.00	0.00	0.00
	C <sub>8</sub> AR.	10.77	10.57	10.98	10.93
	C <sub>9</sub> + PAR.	0.00	0.00	0.00	0.00
	C <sub>9</sub> AR.	9.83	9.74	10.15	10.12
40	C <sub>10</sub> AR.	7.94	7.97	8.22	8.17
	C <sub>10</sub> -C <sub>12</sub> AR.	16.56	16.43	17.20	17.16
	NAPHTHALENE	0.00	0.00	0.00	0.00
	M-NAPHTHALENE	0.00	0.00	0.00	0.00
	C <sub>13</sub> + 'S	0.01	0.00	0.00	0.00
45	WT % CONV, TOTAL	3.68	4.59	3.24	6.40
	TO C <sub>1</sub> -C <sub>4</sub>	1.73	2.62	1.14	1.83
	R+O (CHARGE = 88.8)	90.10	89.90	90.50	90.60
50	1. SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 70; steamed alpha = 10.				
	2. SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 54, steamed alpha = 11.				

TABLE 8

	CATALYST	ZSM-12 <sup>3</sup>
	TEMPERATURE, °C	426
5	(°F)	(799)
	PRESSURE, PSIG	50.00
	kPa	450
	WHSV	10.00
	TIME ON STREAM, HRS.	99.00
10	PRODUCT DIST., WT %	
	C <sub>1</sub>	0.00
	C <sub>2</sub>	0.00
15	C <sub>2</sub> =	0.00
	C <sub>3</sub>	0.00
	C <sub>3</sub> =	0.02
	ISO-C <sub>4</sub>	0.07
	N-C <sub>4</sub>	0.36
	C <sub>4</sub> =	0.58
20	ISO-C <sub>5</sub>	9.63
	N-C <sub>5</sub>	1.51
	C <sub>5</sub> =	3.94
	2,2 DM-C <sub>4</sub>	0.04
	CYCLO-C <sub>5</sub>	0.26
25	2,3 DM-C <sub>4</sub>	0.98
	2-M-C <sub>5</sub>	4.15
	3-M-C <sub>5</sub>	2.66
	N-C <sub>6</sub>	0.75
	C <sub>6</sub> =	1.28
30	M-CYCLO-C <sub>5</sub>	2.66
	BENZENE	1.01
	CYCLO-C <sub>6</sub>	0.33
	C <sub>7</sub> 'S	10.88
	N-C <sub>7</sub>	0.00
35	TOLUENE	5.17
	C <sub>8</sub> 'S	6.36
	N-C <sub>8</sub>	0.00
	C <sub>8</sub> AR.	11.09
	C <sub>9</sub> + PAR.	0.00
	C <sub>9</sub> AR.	10.39
40	C <sub>10</sub> AR.	8.46
	C <sub>10</sub> -C <sub>12</sub> AR.	17.42
	NAPHTHALENE	0.00
	M-NAPHTHALENE	0.00
45	C <sub>13</sub> +'S	0.00
	WT % CONV, TOTAL	3.51
	TO C <sub>1</sub> -C <sub>4</sub>	0.30
	R+O (CHARGE = 88.8)	89.90
50	3. SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 250; alpha = 39.	

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**EXAMPLE 4**

If the mechanism of octane number improvement involves olefin reactions, then as the charge boiling point decreases, the amount of octane improvement should increase due to greater olefin concentration in the front end. Tables 9-11 show the data for distillate-mode FCC gasoline 24 to 154°C (75 to 310°F) (with and without ZSM-5 in the cracking catalyst) and a 24 to 121°C (75 to 250°F) cut of FCC gasoline. These results along with the previous ZSM-12 data on full range FCC and TCC gasolines are plotted in Figure 5.

Table 12 illustrates the effect of boiling range on octane improvement at 0.7% light gas make.

**TABLE 12**

Effect of Boiling Range on

Octane Improvement at 0.7% C<sub>1</sub>-C<sub>4</sub> Make

<u>Charge Stock</u>	<u>Octane Improvement, R+O</u>
24 to 121°C (75 to 250°F) FCC	2.4
24 to 154°C (75 to 310°F) FCC	1.4
24 to 218°C (75 to 425°F) TCC	1.2
24 to 218°C (75 to 425°F) FCC	1.0

The results are in line with expectation. Yield octane number improves in the order 24 to 121°C (75 to 250°F), 24 to 154°C (75 to 310°F), 24 to 218°C (75 to 425°F). The 24 to 154°C (75 to 310°F) distillate-mode FCC gasoline made with ZSM-5 as a cracking additive is improved about 0.5 R+O. However, some other reactions apparently occur in the cracking step and the amount of octane number improvement in subsequent processing is thus limited.

The amount of octane number improvement with the lighter charges is 1.5 to 2.5 R+O per 1% C<sub>1</sub>-C<sub>4</sub> make. This is very efficient octane production and suggests that the economics would be most favorable in a situation where the end boiling point of the TCC gasoline is under 177°C (350°F) to maximize distillate.

**EXAMPLE 5**

A full range FCC gasoline was converted over ZSM-5 and ZSM-12 at varying process conditions. Results are shown in Tables 13-15 and Fig. 6.

It would be convenient if the reaction would occur at the temperature that gasoline is taken off the distillation tower. However, the results show that no octane number improvement is obtained until approximately 0.5% conversion to C<sub>1</sub>-C<sub>4</sub> takes place, and this does not occur until approximately 343°C (650°F). Thus low temperature operation is not possible unless nitrogen poisons are removed by preadsorption in a guard chamber, solvent extraction or other conventional means. In this mode of operation, use of more acidic zeolites (alpha of 100-500), or more catalyst (space velocities of 1 to 5 WHSV) may be used to achieve the desired conversion at lower temperatures. Temperatures as low as 260°C (500°F) will work, but preferably reaction temperatures are at least 316°C (600°F) to 343°C (650°F), most preferably above 371°C (700°F).

Increasing pressure is detrimental to octane improvement. Coking is severe at higher pressure and probably some oligomerization occurs since there is an increase in heavy ends. No octane improvement results and in fact a decrease occurs. For most gasolines, the pressure should be below 1500 kPa (200 psig), and preferably the reaction is conducted at atmospheric to 310 kPa (30 psig). Operation under a vacuum or with a diluent will help.

Adding hydrogen to the system does not influence the reaction or the yield octane. Without metal, no hydrogenation occurs in the olefinic light gases. This also suggests that hydrogen will not affect aging.

TABLE 9

5	CATALYST	ZSM-12 <sup>1</sup>	ZSM-12	
	TEMPERATURE, °C	427	4821	
	(°F)	(800)	(900)	
	PRESSURE, PSIG	30.00	30.00	
	kPa	310	310	
	WHSV	10.00	10.00	
10	TIME ON STREAM, HRS.	21.80	108.70	
	PRODUCT DIST., WT %			
	C <sub>1</sub>	0.05	0.03	CHARGE
	C <sub>2</sub>	0.01	0.14	DISTILLATE-MODE
15	C <sub>2</sub> =	0.02	0.07	FCC GASOLINE
	C <sub>3</sub>	0.02	0.08	
	C <sub>3</sub> =	0.32	0.29	
	ISO-C <sub>4</sub>	0.00	0.01	0.01
	N-C <sub>4</sub>	0.03	0.12	0.13
20	C <sub>4</sub> =	0.97	0.79	0.56
	ISO-C <sub>5</sub>	1.92	1.75	1.88
	N-C <sub>5</sub>	0.10	0.08	-
	C <sub>5</sub> =	10.30	9.96	10.73
	2,2 DM-C <sub>4</sub>	0.10	0.15	0.12
	CYCLO-C <sub>5</sub>	0.64	0.67	0.83
25	2,3 DM-C <sub>4</sub>	0.44	0.51	0.60
	2-M-C <sub>5</sub>	2.11	2.09	2.03
	3-M-C <sub>5</sub>	0.64	0.63	0.62
	N-C <sub>6</sub>	0.00	0.00	-
	C <sub>6</sub> =	8.51	8.50	8.78
30	M-CYCLO-C <sub>5</sub>	2.55	2.47	2.27
	BENZENE	2.82	2.83	2.95
	CYCLO-C <sub>6</sub>	0.42	0.38	0.46
	C <sub>7</sub> 'S	16.39	16.82	16.55
	N-C <sub>7</sub>	0.00	0.00	-
35	TOLUENE	5.70	5.62	5.54
	C <sub>8</sub> 'S	14.04	14.11	14.14
	N-C <sub>8</sub>	0.00	0.00	-
	C <sub>8</sub> AR.	10.91	10.71	10.35
	C <sub>9</sub> + PAR.	0.00	0.00	-
	C <sub>9</sub> AR.	20.98	21.20	21.45
40	C <sub>10</sub> AR.	0.00	0.00	100.00
	C <sub>10</sub> -C <sub>12</sub> AR.	0.00	0.00	
	NAPHTHALENE	0.00	0.00	
	M-NAPHTHALENE	0.00	0.00	
	C <sub>13</sub> + 'S	0.00	0.00	
45	WT % CONV, TOTAL	3.53	2.79	
	TO C <sub>1</sub> -C <sub>4</sub>	0.98	1.00	
	R+O (CHARGE = 91.1)	93.30	92.60	
50	1. Steamed alpha = 11.			

TABLE 10

5	CATALYST	ZSM-12 <sup>2</sup>	ZSM-12	
	TEMPERATURE °C	427	454	
5	(°F)	(801)	(850)	
	PRESSURE, PSIG	30.00	30.00	
5	kPa	310	310	
	WHSV	10.00	10.00	
5	TIME ON STREAM, HRS.	23.30	92.50	
10	PRODUCT DIST., WT %			
15	C <sub>1</sub>	0.00	0.00	DISTILLATE MODE FCC GASOLINE (H-ZSM-5 ADDITIVE IN CRACKING CATALYST)
	C <sub>2</sub>	0.01	0.03	
15	C <sub>2</sub> =	0.02	0.02	
	C <sub>3</sub>	0.01	0.02	
15	C <sub>3</sub> =	0.46	0.30	
	ISO-C <sub>4</sub>	0.01	0.00	
15	N-C <sub>4</sub>	0.05	0.01	0.03
	C <sub>4</sub> =	0.89	0.66	
20	ISO-C <sub>5</sub>	3.18	3.15	0.26
	N-C <sub>5</sub>	0.09	0.09	
20	C <sub>5</sub> =	15.41	15.35	3.21
	2,2 DM-C <sub>4</sub>	0.08	0.03	
20	CYCLO-C <sub>5</sub>	0.56	1.35	15.91
	2,3 DM-C <sub>4</sub>	0.60	0.00	
25	2-M-C <sub>5</sub>	3.59	3.57	1.47
	3-M-C <sub>5</sub>	1.14	1.16	
25	N-C <sub>6</sub>	0.00	0.00	3.61
	C <sub>6</sub> =	9.30	9.48	
25	M-CYCLO-C <sub>5</sub>	3.70	3.62	1.16
	BENZENE	2.69	2.69	
30	CYCLO-C <sub>6</sub>	0.00	0.00	2.81
	C <sub>7</sub> 'S	14.95	15.23	
30	N-C <sub>7</sub>	0.00	0.00	15.33
	TOLUENE	5.39	5.27	
35	C <sub>8</sub> 'S	11.00	11.07	5.14
	N-C <sub>8</sub>	0.00	0.00	
35	C <sub>8</sub> AR.	8.44	8.51	11.15
	C <sub>9</sub> + PAR.	0.00	0.00	
35	C <sub>9</sub> AR.	18.43	18.37	8.27
	C <sub>10</sub> AR.	0.00	0.00	
40	C <sub>10</sub> -C <sub>12</sub> AR.	0.00	0.00	18.50
	NAPHTHALENE	0.00	0.00	
40	M-NAPHTHALENE	0.00	0.00	100.00
	C <sub>13</sub> + 'S	0.00	0.00	
45	WT % CONV, TOTAL	2.68	1.50	
	TO C <sub>1</sub> -C <sub>4</sub>	1.20	0.85	
45	R+O (CHARGE = 93.5)	94.50	94.40	

2. Steamed alpha = 11.

TABLE 11

6	CATALYST	ZSM-12 <sup>3</sup>	ZSM-12	ZSM-12	
	TEMPERATURE, °C	399	427	482	
6	(°F)	(750)	(801)	(900)	
6	PRESSURE, PSIG	30.00	30.00	30.00	
	kPa	310	310	310	
6	WHSV	10.00	10.00	10.00	
6	TIME ON STREAM, HRS.	21.30	69.00	114.70	
10	PRODUCT DIST., WT %				
15	C <sub>1</sub>	0.00	0.00	0.01	
	C <sub>2</sub>	0.00	0.01	0.06	
15	C <sub>2</sub> =	0.01	0.00	0.03	*FCC
15	C <sub>3</sub>	0.00	0.00	0.03	GASOLINE
	C <sub>3</sub> =	0.30	0.02	0.07	
15	ISO-C <sub>4</sub>	0.02	0.01	0.01	0.01
	N-C <sub>4</sub>	0.21	0.21	0.20	
20	C <sub>4</sub> =	0.88	0.43	0.48	0.37
	ISO-C <sub>5</sub>	7.53	7.88	7.56	
20	N-C <sub>5</sub>	0.24	0.21	0.24	-
	C <sub>5</sub> =	14.37	15.82	15.40	
20	2,2 DM-C <sub>4</sub>	0.07	0.12	0.14	15.84
	CYCLO-C <sub>5</sub>	1.43	1.62	1.70	
25	2,3 DM-C <sub>4</sub>	1.15	1.21	1.20	1.70
	2-M-C <sub>5</sub>	6.91	7.26	7.33	
25	3-M-C <sub>5</sub>	3.62	3.85	3.86	7.35
	N-C <sub>6</sub>	2.67	2.56	2.61	
25	C <sub>6</sub> =	7.17	9.06	8.98	2.68
	M-CYCLO-C <sub>5</sub>	5.76	5.89	5.88	
30	BENZENE	3.49	3.87	3.84	5.70
	CYCLO-C <sub>6</sub>	0.86	0.86	0.88	
30	C <sub>7</sub> 'S	20.31	22.72	22.91	0.91
	N-C <sub>7</sub>	0.00	0.00	0.00	
35	TOLUENE	7.44	7.97	8.26	22.68
	C <sub>8</sub> 'S	13.50	7.00	6.94	
35	N-C <sub>8</sub>	0.00	0.00	0.00	8.01
	C <sub>8</sub> AR.	1.19	1.20	1.25	
35	C <sub>9</sub> + PAR.	0.00	0.00	0.00	6.92
	C <sub>9</sub> AR.	0.30	0.14	0.11	
40	C <sub>10</sub> AR.	0.22	0.02	0.02	0.09
	C <sub>10</sub> -C <sub>12</sub> AR.	0.30	0.01	0.01	
40	NAPHTHALENE	0.00	0.00	0.00	0.03
	M-NAPHTHALENE	0.00	0.00	0.00	
40	C <sub>13</sub> + 'S	0.00	0.00	0.00	0.04
45	WT % CONV, TOTAL	8.48	1.53	1.88	100.00
	TO C <sub>1</sub> -C <sub>4</sub>	0.86	0.21	0.37	
45	R+O (CHARGE = 89.8)	92.80	92.20	92.10	

3. Steamed alpha = 13.

\*FCC Gasoline = 24 to 121°C (75 to 250°F)



## FULL RANGE FCC GASOLINE OVER STEAMED H-ZSM-5, ALPHA - 10

TABLE 13

5	CATALYST	ZSM-5	ZSM-5	ZSM-5
	TEMPERATURE, °C	149	260	343
	(°F)	(301)	(501)	(650)
	PRESSURE, PSIG	30.00	30.00	30.00
	kPa	310	310	310
10	WHSV	10.00	10.00	10.00
	TIME ON STREAM, HRS.	20.80	44.20	66.00
	PRODUCT DIST., WT %			
	C <sub>1</sub>	0.00	0.00	0.00
15	C <sub>2</sub>	0.00	0.00	0.00
	C <sub>2</sub> <sup>=</sup>	0.00	0.00	0.00
	C <sub>3</sub>	0.00	0.00	0.00
	C <sub>3</sub> <sup>=</sup>	0.01	0.00	0.05
	ISO-C	0.03	0.03	0.03
20	N-C <sub>4</sub>	0.15	0.16	0.17
	C <sub>4</sub> <sup>=</sup>	0.41	0.39	0.47
	ISO-C <sub>5</sub>	7.17	7.20	7.13
	N-C <sub>5</sub>	0.22	0.24	0.23
	C <sub>5</sub> <sup>=</sup>	8.28	8.32	8.37
25	2,2 DM-C <sub>4</sub>	0.07	0.09	0.08
	CYCLO-C <sub>5</sub>	0.72	0.73	0.33
	2,3 DM-C <sub>4</sub>	0.66	0.66	0.90
	2-M-C <sub>5</sub>	3.88	3.91	3.80
	3-M-C <sub>5</sub>	2.13	2.15	2.13
	N-C <sub>6</sub>	0.99	0.98	0.95
30	C <sub>6</sub> <sup>=</sup>	3.46	3.51	3.40
	M-CYCLO-C <sub>5</sub>	2.63	2.67	2.70
	BENZENE	1.53	1.47	1.52
	CYCLO-C <sub>6</sub>	0.23	0.32	0.25
	C <sub>7</sub> 'S	11.74	11.99	11.91
35	N-C <sub>7</sub>	0.00	0.00	0.00
	TOLUENE	4.77	4.84	4.77
	C <sub>8</sub> 'S	6.53	6.70	6.73
	N-C <sub>8</sub>	0.00	0.00	0.00
	C <sub>8</sub> AR.	10.13	10.11	10.06
	C <sub>9</sub> + PAR.	0.00	0.00	0.00
40	C <sub>9</sub> AR.	10.16	10.08	10.12
	C <sub>10</sub> AR.	8.77	8.65	8.74
	C <sub>10</sub> -C <sub>12</sub> AR.	15.26	14.79	15.16
	NAPHTHALENE	0.00	0.00	0.00
	M-NAPHTHALENE	0.00	0.00	0.00
45	C <sub>13</sub> + 'S	0.01	0.01	0.00
	WT % CONV, TOTAL	2.43	2.03	3.24
	TO C <sub>1</sub> -C <sub>4</sub>	0.12	0.11	0.25
	R+O (CHARGE = 89.3)	89.10	88.90	89.40

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## FULL RANGE FCC GASOLINE OVER STEAMED H-ZSM-5, ALPHA - 10

TABLE 14

5	CATALYST	ZSM-5	ZSM-5	ZSM-5
	TEMPERATURE, °C	373	371	386
	(°F)	(704)	(700)	(726)
	PRESSURE, PSIG	400.00	400.00	200.00
	kPa	2900	2900	1500
10	WHSV	10.00	10.00	10.00
	TIME ON STREAM, HRS.	25.80	45.30	73.80
	PRODUCT DIST., WT %			
	C <sub>1</sub>	0.00	0.00	0.00
15	C <sub>2</sub>	0.00	0.00	0.00
	C <sub>2</sub> =	0.02	0.01	0.01
	C <sub>3</sub>	0.00	0.00	0.00
	C <sub>3</sub> =	0.30	0.16	0.31
	ISO-C <sub>4</sub>	0.03	0.02	0.03
20	N-C <sub>4</sub>	0.18	0.14	0.19
	C <sub>4</sub> =	0.65	0.47	0.69
	ISO-C <sub>5</sub>	6.70	6.41	6.94
	N-C <sub>5</sub>	0.16	0.17	0.19
	C <sub>5</sub> =	6.90	7.09	7.61
25	2,2 DM-C <sub>4</sub>	0.03	0.02	0.03
	CYCLO-C <sub>5</sub>	0.57	0.59	0.62
	2,3 DM-C <sub>4</sub>	0.71	0.65	0.70
	2-M-C <sub>5</sub>	3.79	3.67	3.81
	3-M-C <sub>5</sub>	0.11	2.04	2.09
	N-C <sub>6</sub>	1.05	1.05	1.01
30	C <sub>6</sub> =	2.88	3.00	3.12
	M-CYCLO-C <sub>5</sub>	2.73	2.88	2.74
	BENZENE	1.40	1.37	1.44
	CYCLO-C <sub>6</sub>	0.47	0.38	0.44
	C <sub>7</sub> 'S	11.56	11.62	11.62
35	N-C <sub>7</sub>	0.00	0.00	0.00
	TOLUENE	4.68	4.78	4.76
	C <sub>8</sub> 'S	7.06	7.08	6.99
	N-C <sub>8</sub>	0.00	0.00	0.00
	C <sub>8</sub> AR.	10.32	10.43	10.25
	C <sub>9</sub> + PAR.	0.00	0.00	0.00
40	C <sub>9</sub> AR.	10.53	10.71	10.29
	C <sub>10</sub> AR.	9.36	9.40	8.96
	C <sub>10</sub> -C <sub>12</sub> AR.	15.89	16.05	15.15
	NAPHTHALENE	0.00	0.00	0.00
	M-NAPHTHALENE	0.00	0.00	0.00
45	C <sub>13</sub> + 'S	0.00	0.00	0.00
	WT % CONV, TOTAL	4.08	4.21	2.81
	TO C <sub>1</sub> -C <sub>4</sub>	0.63	0.31	0.65
	R+O (CHARGE = 89.2)	88.80	89.30	89.20

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REACTION OF FULL RANGE FCC GASOLINE OVER STEAMED  
H-ZSM-12, ALPHA = 11

TABLE 15

5	CATALYST	ZSM-12	ZSM-12
	TEMPERATURE, °C	482	461
	(°F)	(899)	(861)
	PRESSURE, PSIG	30.00	30.00
10	kPa	310	310
	WHSV	10.00	10.00
	H <sub>2</sub> /HC	2.10	2.10
	TIME ON STREAM, HRS.	23.50	95.50
15	PRODUCT DIST., WT %		
	C <sub>1</sub>	0.00	0.00
	C <sub>2</sub>	0.04	0.01
	C <sub>2</sub> =	0.07	0.01
	C <sub>3</sub>	0.03	0.01
20	C <sub>3</sub> =	1.60	0.33
	ISO-C <sub>4</sub>	0.04	0.02
	N-C <sub>4</sub>	0.28	0.16
	C <sub>4</sub> =	2.10	0.84
	ISO-C <sub>5</sub>	6.84	6.58
25	N-C <sub>5</sub>	0.17	0.13
	C <sub>5</sub> =	8.68	8.08
	2,2 DM-C <sub>4</sub>	0.08	0.10
	CYCLO-C <sub>5</sub>	0.67	0.67
	2,3 DM-C <sub>4</sub>	0.66	0.68
	2-M-C <sub>5</sub>	3.96	3.96
30	3-M-C <sub>5</sub>	2.13	2.15
	N-C <sub>6</sub>	1.10	1.10
	C <sub>6</sub> =	3.07	3.28
	M-CYCLO-C <sub>5</sub>	2.76	2.79
	BENZENE	1.46	1.51
35	CYCLO-C <sub>6</sub>	0.30	0.33
	C <sub>7</sub> 'S	10.83	12.00
	N-C <sub>7</sub>	0.00	0.00
	TOLUENE	4.72	4.76
	C <sub>8</sub> 'S	5.91	6.66
40	N-C <sub>8</sub>	0.00	0.00
	C <sub>8</sub> AR.	9.89	10.08
	C <sub>9</sub> + PAR.	0.00	0.00
	C <sub>9</sub> AR.	9.66	9.99
	C <sub>10</sub> AR.	8.42	8.73
	C <sub>10</sub> -C <sub>12</sub> AR.	14.59	15.05
45	NAPHTHALENE	0.00	0.00
	M-NAPHTHALENE	0.00	0.00
	C <sub>13</sub> + 'S	0.00	0.00
50	WT % CONV, TOTAL	5.37	3.44
	TO C <sub>1</sub> -C <sub>4</sub>	3.37	0.76
	R+O (CHARGE = 89.1)	91.10	90.00

**EXAMPLE 6**

In order to determine the olefin content of the cracked gases, a full range FCC gasoline was converted over a steamed ZSM-5 catalyst. Composition of the product is shown in Table 16.

5 While the amount of light gas produced is small, it is primarily C<sub>3</sub>-C<sub>4</sub> olefins which can be used to increase alkylate yield.

The C<sub>6</sub>+ yield is 98.1 vol.% with 1.5 wt.% C<sub>1</sub>-C<sub>4</sub> make. The volume of isobutane required for alkylation is 2.8%, giving a gasoline plus alkylate yield of 102.2+ vol.%.

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TABLE 16

5	CATALYST	ZSM-5
	TEMPERATURE, °C	384
	(°F)	(724)
	PRESSURE, PSIG	30.00
	kPa	170
	WHSV	10.00
10	TIME ON STREAM, HRS.	119.00
	PRODUCT DIST., WT %	
	C <sub>1</sub>	0.00
15	C <sub>2</sub>	0.00
	C <sub>2</sub> =	0.02
	C <sub>3</sub>	0.00
	C <sub>3</sub> =	0.48
	ISO-C <sub>4</sub>	0.03
20	N-C <sub>4</sub>	0.22
	C <sub>4</sub> =	1.05
	ISO-C <sub>5</sub>	6.15
	N-C <sub>5</sub>	0.21
	C <sub>5</sub> =	10.19
	2,2 DM-C <sub>4</sub>	0.00
25	CYCLO-C <sub>5</sub>	0.86
	2,3 DM-C <sub>4</sub>	0.55
	2-M-C <sub>5</sub>	3.30
	3-M-C <sub>5</sub>	1.69
	N-C <sub>6</sub>	1.21
30	C <sub>6</sub> =	3.77
	M-CYCLO-C <sub>5</sub>	2.82
	BENZENE	1.78
	CYCLO-C <sub>6</sub>	0.47
	C <sub>7</sub> 'S	11.24
35	N-C <sub>7</sub>	0.00
	TOLUENE	4.87
	C <sub>8</sub> 'S	6.45
	N-C <sub>8</sub>	0.00
	C <sub>8</sub> AR.	8.96
	C <sub>9</sub> + PAR.	0.00
40	C <sub>9</sub> AR.	10.10
	C <sub>10</sub> AR.	8.37
	C <sub>10</sub> -C <sub>12</sub> AR.	15.21
	NAPHTHALENE	0.00
	M-NAPHTHALENE	0.00
45	C <sub>13</sub> + 'S	0.00
	WT % CONV, TOTAL	2.95
	TO C <sub>1</sub> -C <sub>4</sub>	1.12
50	R+O (CHARGE = 91.4)	92.80

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### Claims

- 5 1. A process for improving the octane number of gasoline characterised by contacting a gasoline containing at least 20 wt.% olefins with an acidic crystalline zeolite catalyst having an alpha value of 5 to 100 and a Constraint Index of 1 to 12 in the absence of hydrogen at 343 to 510°C (650 to 950°F) at a pressure of from atmospheric to 450 kPa to effect a conversion of less than 5 wt.% to C<sub>1</sub>-C<sub>4</sub> products and increase the octane number of the gasoline.
- 10 2. The process of claim 1 further characterised in that the WHSV of gasoline contact is 0.1 to 20 and the octane number of the gasoline product is increased by at least 1.0 octane number for every 2.0 wt.% loss of gasoline boiling range products.
3. The process of claim 2 wherein the octane number of the product increases at least 1.0 for every 1.0 wt.% loss of gasoline boiling range material.
- 15 4. The process of any preceding claim further characterised in that the zeolite is selected from the group of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48.
5. The process of any preceding claim further characterised in that the temperature is 371 to 482°C (700 to 900°F).
- 20 6. The process of any preceding claim further characterised in that the gasoline feed contains at least 30% by weight olefins.
7. The process of any preceding claim further characterised in that the gasoline contacts the zeolite in a fixed bed, at a weight hourly space velocity of 5 to 10.
8. The process of any preceding claim further characterised in that the zeolite has an alpha value of 10 to 50.

### Ansprüche

- 30 1. Verfahren zur Erhöhung der Oktanzahl von Benzin, gekennzeichnet durch den Kontakt von Benzin, der mindestens 20 Gew.-% Olefine enthält, mit einem sauren kristallinen Zeolithkatalysator, der einen Alpha-Wert von 5 bis 100 und einen Zwangsindex von 1 bis 12 aufweist, in Abwesenheit von Wasserstoff bei 343 bis 510°C (650 bis 950°F) bei einem Druck von atmosphärischem Druck bis 450 kPa, um die Umwandlung von weniger als 5 Gew.-% in C<sub>1</sub>-C<sub>4</sub>-Produkte durchzuführen und die Oktanzahl des Benzins zu erhöhen.
- 35 2. Verfahren nach Anspruch 1, weiterhin dadurch gekennzeichnet, daß die WHSV des Benzinkontaktes 0,1 bis 20 beträgt und die Oktanzahl des Benzinproduktes für jeweils 2,0 Gew.-% Verlust der Produkte des Benzinsiedebereichs um mindestens 1,0 Oktanzahl erhöht wird.
3. Verfahren nach Anspruch 2, worin die Oktanzahl des Produktes für jeweils 1,0 Gew.-% Verlust des Materials des Benzinsiedebereichs um mindestens 1,0 steigt.
- 40 4. Verfahren nach einem der vorstehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß der Zeolit aus der Gruppe von ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 und ZSM-48 ausgewählt ist.
5. Verfahren nach einem der vorstehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß die Temperatur 371 bis 482°C (700 bis 900 °F) beträgt.
- 45 6. Verfahren nach einem der vorstehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß die Benzinzufuhr mindestens 30 Gew.-% Olefine enthält.
7. Verfahren nach einem der vorstehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß das Benzin bei einer stündlichen Gewichts-Raum-Geschwindigkeit von 5 bis 10 in einem Festbett mit dem Zeolith in Kontakt kommt.
- 50 8. Verfahren nach einem der vorstehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß der Zeolith einen Alpha-Wert von 10 bis 50 aufweist.

### Revendications

- 55 1. Un procédé pour augmenter l'indice d'octane de l'essence, caractérisé en ce qu'il consiste à mettre en contact une essence contenant au moins 20% en poids d'oléfinés avec un catalyseur à base d'une zéolite cristalline acide ayant un indice alpha de 5 à 100 et un indice de contrainte de 1 à 12, en l'absence d'hydro-

gène à une température de 343 à 510°C (650 à 950°F) sous une pression comprise entre la pression atmosphérique et 450 kPa, pour provoquer une conversion de moins de 5% en poids donnant des produits en C<sub>1</sub>-C<sub>4</sub>, et augmenter l'indice d'octane de l'essence.

5 2. Le procédé selon la revendication 1, caractérisé en outre en ce que la vitesse spatiale horaire pondérale du contact de l'essence est de 0,1 à 20, et que l'indice d'octane de l'essence obtenue augmente d'environ 1,0 unité d'indice d'octane pour chaque 2,0% en poids de perte des produits ayant l'intervalle d'ébullition de l'essence.

3. Le procédé selon la revendication 2, dans lequel l'indice d'octane du produit augmente d'au moins 1,0 unité pour 1,0% en poids de perte du produit ayant l'intervalle d'ébullition de l'essence.

10 4. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que la zéolite est choisie dans le groupe comprenant la ZSM-5, la ZSM-11, la ZSM-12, la ZSM-23, la ZSM-35, la ZSM-38, la ZSM-48.

5. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que la température est de 371 à 482°C (700 à 900°F).

15 6. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que l'essence de charge contient au moins 30% en poids d'oléfin.

7. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que l'essence entre en contact avec la zéolite dans un lit fixe, à une vitesse spatiale horaire pondérale de 5 à 10.

20 8. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que la zéolite a un indice alpha de 10 à 50.

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FIG. 1

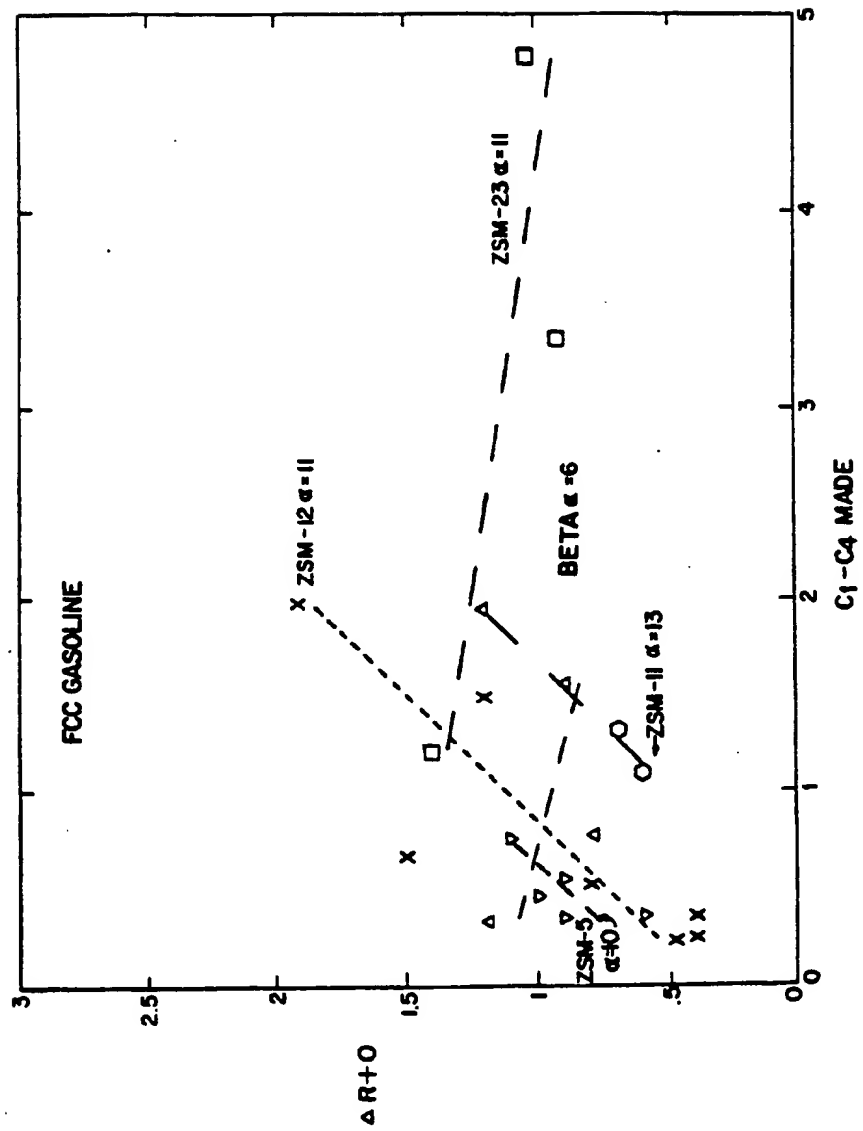




FIG.2

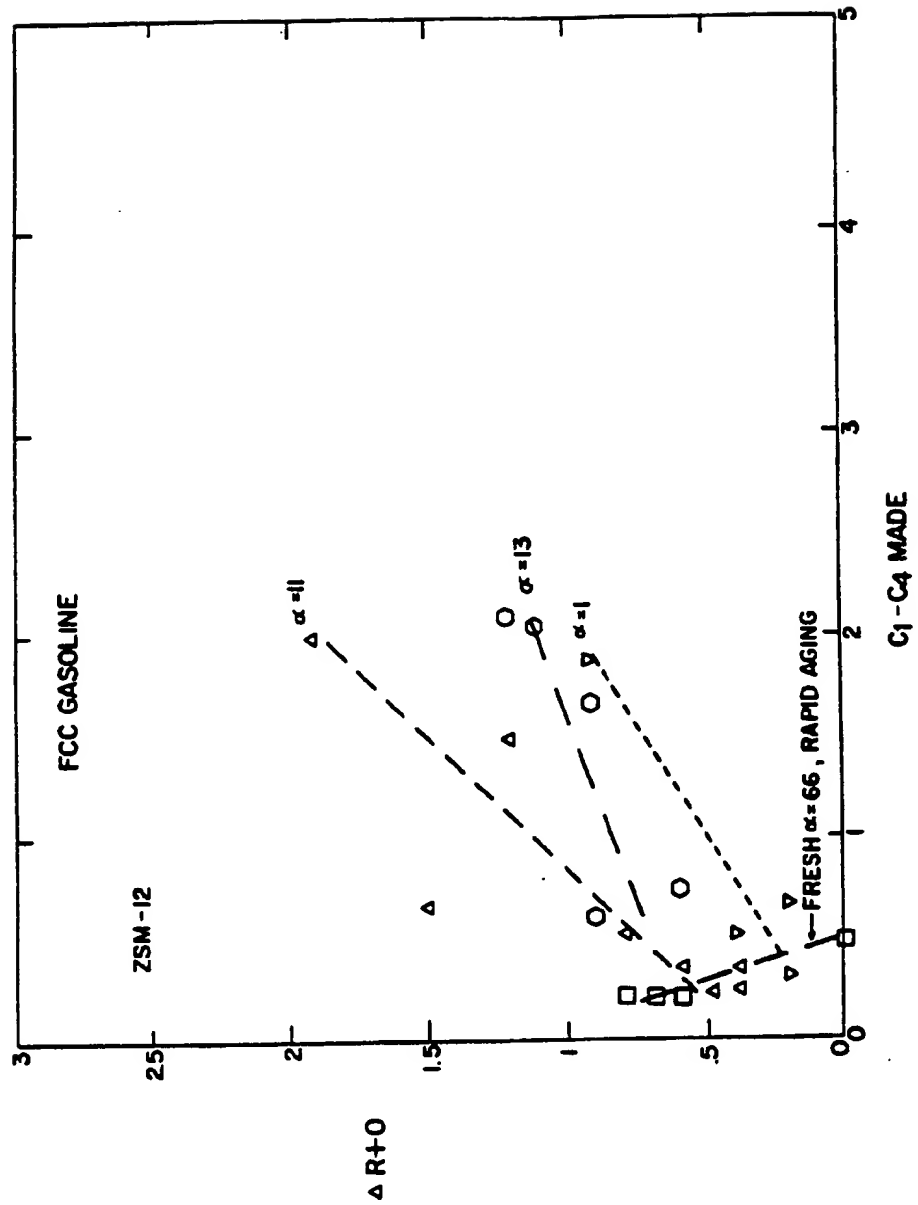


FIG.3

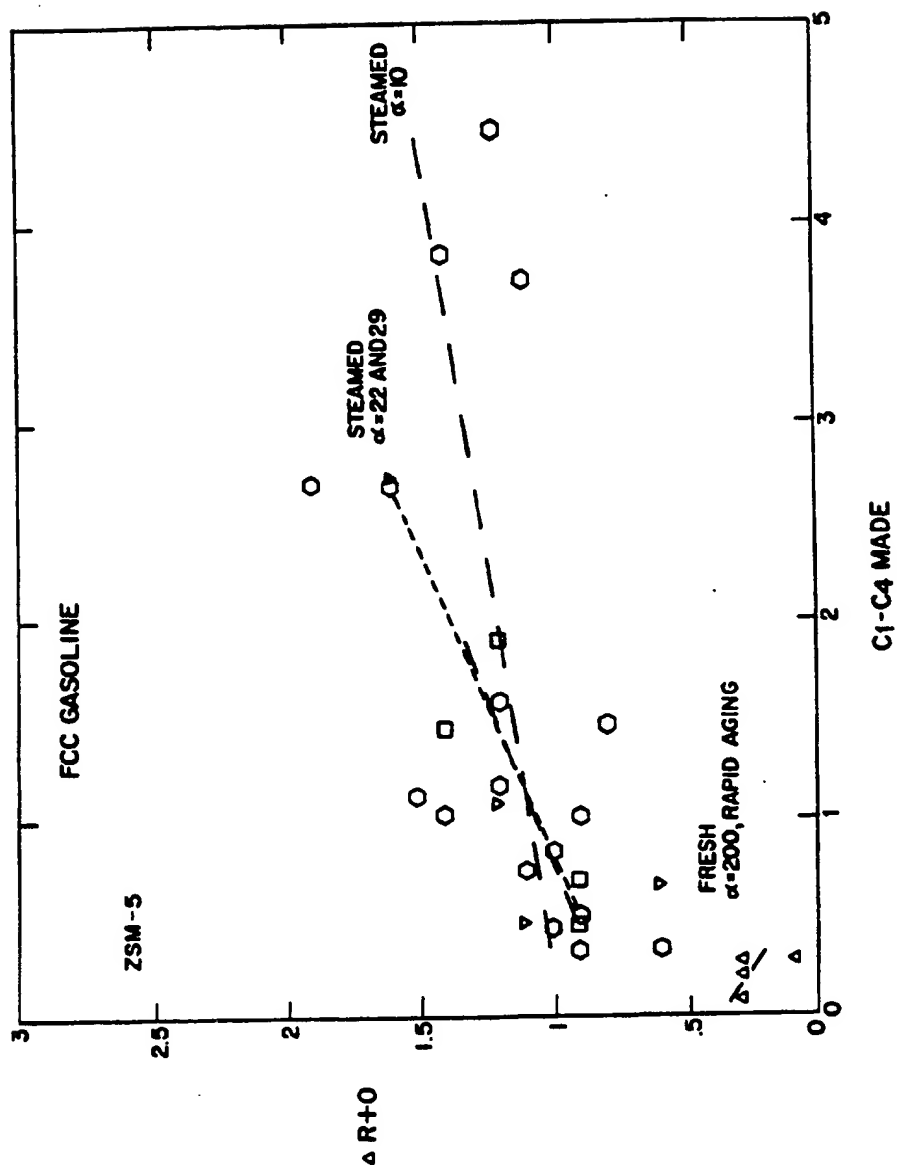


FIG. 4

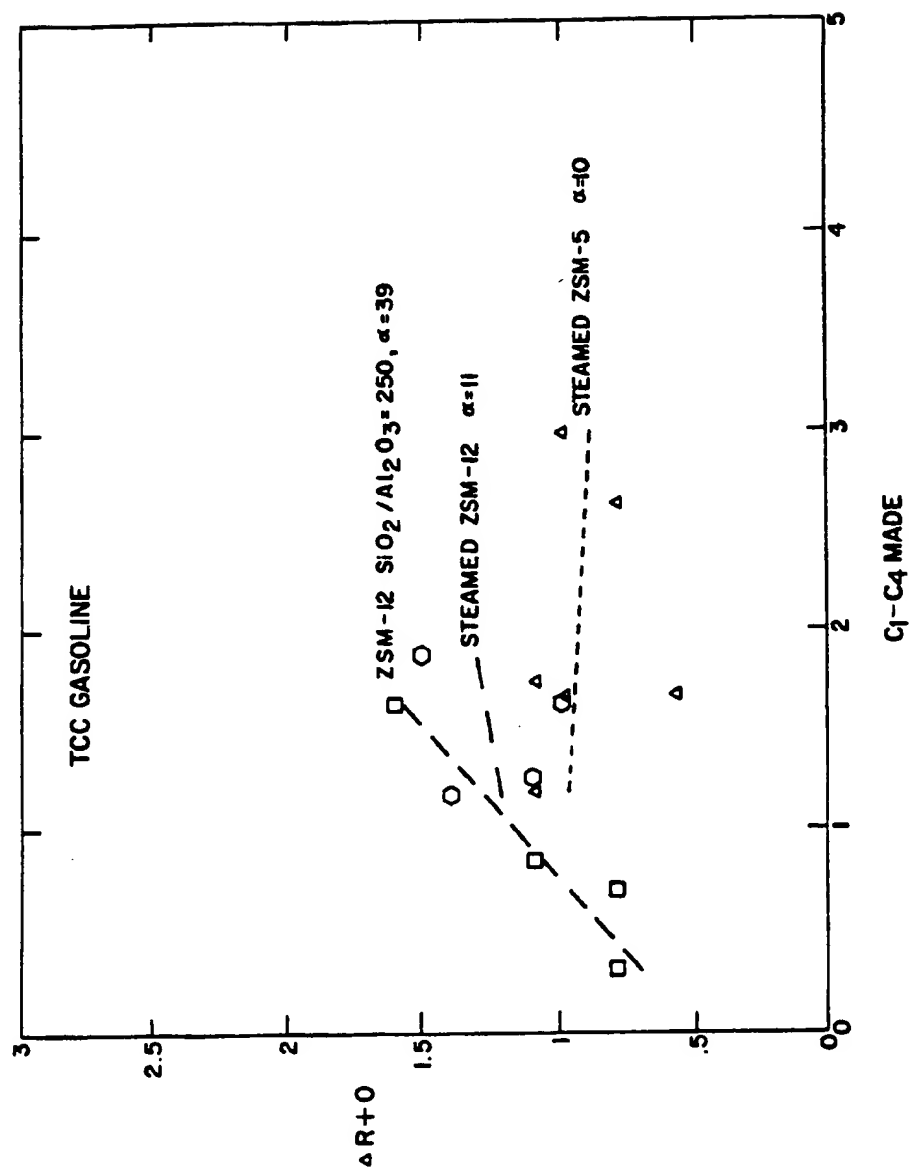


FIG. 5

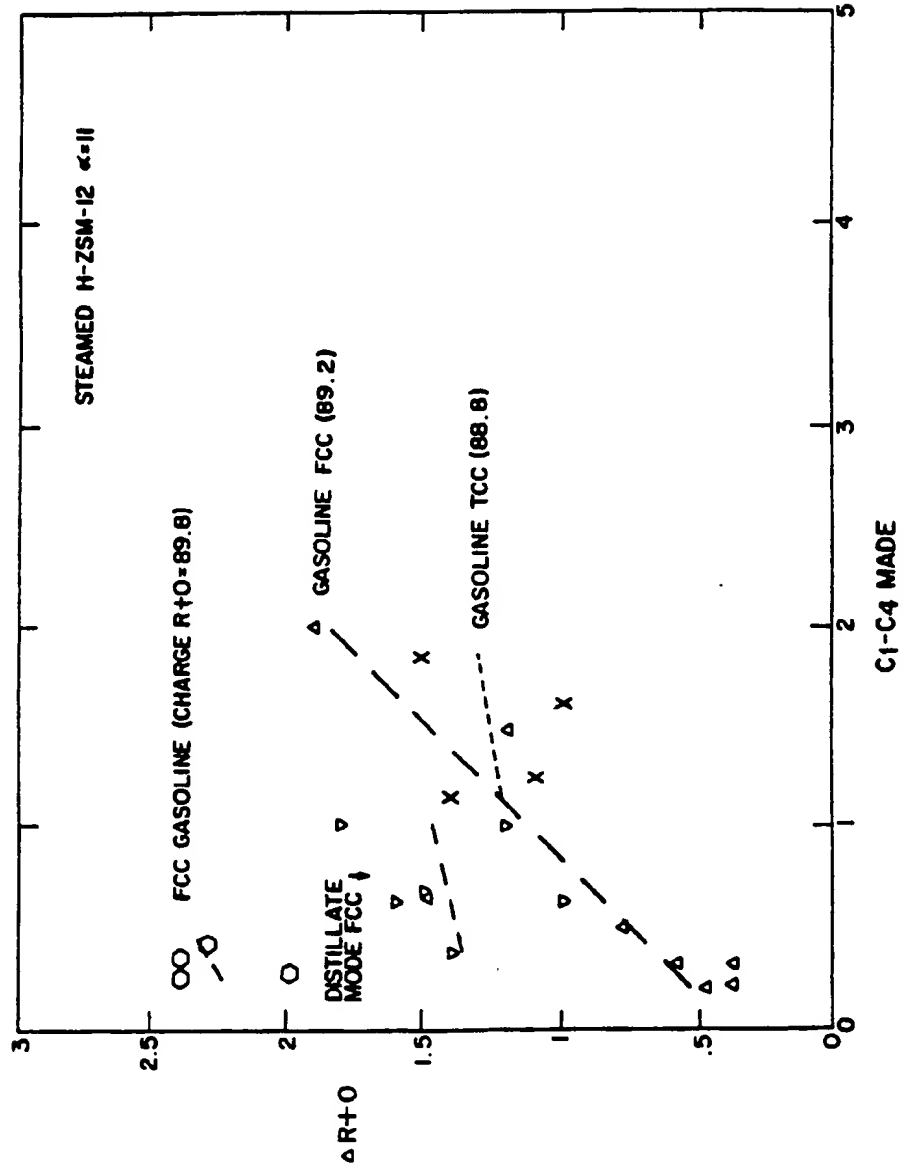


FIG. 6

